CORE-XI

Quantum Mechanics and applications:

Wave function:-

The de-broglie's relation is given by $\lambda = h/p$ for a moving particle like photon, electron etc. This suggest that localized particles & photons are possible to be represented by a wave function $\psi(\vec{r},t)$, $\psi(\vec{r},t)$ is the associated de broglie's wave function of a moving particle and is function of space($\vec{r}$) and time(t), which gives nearly complete information about the state of a physical system of a particular time.

The value of state function $\psi(\vec{r},t)$ at a particular point ($\vec{r}$) and at a particular time t represents the probability of finding the particle at that point r in time t. to find out the nature of wave function $\psi(\vec{r},t)$. Let us assume that

1. Quantum mechanical particle is free. i.e external force are absent
2. The motion is non-relativistic and one dimensional, say along x-axis.

If 'p' be the momentum & 'E' be the energy of the particle then the debroglie wavelength is

$$\lambda = h/p$$

$$\gamma = E/h$$

The wave vector is $k = 2\pi/\lambda$

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$\Rightarrow k = \frac{2\pi p}{h}$

$\Rightarrow k = \frac{p}{\hbar} \quad \left(\hbar = \frac{h}{2\pi} \right)$ ——— (1)

The angular frequency $\omega = 2\pi\nu$

$$\omega = \frac{2\pi E}{h}$$

$$\omega = \frac{E}{\hbar} \quad \text{——— (2)}$$

Since the particle is free, so

$\Rightarrow E = \frac{p^2}{2m}$

$\Rightarrow p = \sqrt{2mE}$

$\Rightarrow k = \frac{p}{\hbar} = \sqrt{\frac{2mE}{\hbar}}$ ——— (3)

The possible harmonic waves representing a particle travelling along x-axis are given by,

$\psi_1 = a \sin(\omega t - kx)$

or $y = a \cos(\omega t - ax)$ ——— (4)

$\psi_2 = A e^{-i(\omega t + kx)}$

~~$\psi_2 = A e^{i(kx - \omega t)}$~~

or $\psi_2 = A e^{i(kx - \omega t)}$ ——— (5)

The waves represented by eqn (4) are real but those represented by eqn (5) are complex. as

$e^{-i(\omega t - kx)} = \cos(\omega t - kx) - i \sin(\omega t - kx)$ ——— (6)

& $e^{i(\omega t + kx)} = \cos(\omega t - kx) + i \sin(\omega t - kx)$ ——— (7)

eqn (6) and (7) shows that.

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The complex waves are the coherent combinations of real waves with a complex co-efficient.

Let, a particle travelling along positive x-axis be represented by $\psi_1 =$

$\psi_1 = a \sin(\omega t - kx)$

and particle travelling along (-x) axis is

$\psi_1' = a \sin(\omega t + kx)$

According to superposition principle

$\Rightarrow \psi = \psi_1 + \psi_2'$

$\Rightarrow \psi = a \sin(\omega t - kx) + a \sin(\omega t + kx)$

$\Rightarrow \psi = 2a \sin(\omega t) \cdot \cos(kx)$ ——— (8)

At, $t = 0$, $\psi = 0$

i.e the wave function vanishes which means probability of finding the particle is zero everywhere.

As the particle cannot disappear everywhere we conclude that eqn (8) cannot represent a moving particle & hence wave represented by eqn (4) cannot represent a particle in motion.

But the waves $\psi_2 = A e^{-i(\omega t - kx)}$

& $\psi_2' = A e^{-i(\omega t + kx)}$

representing particles travelling along +ve and -ve axis and by superposition principle,

$\psi = \psi_2 + \psi_2'$

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$\Rightarrow \psi = A e^{-i(\omega t - kx)} + A e^{-i(\omega t + kx)}$

$\Rightarrow \psi = 2A e^{-i\omega t} \cos kx$ ——— (9)

At, $t=0$, $\psi = 2A \cos kx$

i.e ψ does not vanish identically everywhere & it is an acceptable wave function representing a moving particle.

Thus the acceptable wave function is,

$\psi = A e^{-i(\omega t - kx)}$ ——— (10)

putting values of ω & k in eqn (10)

$\Rightarrow \psi = A e^{-i\left(\frac{Et}{\hbar} - \frac{\sqrt{2mE}}{\hbar} x\right)}$ ——— (11)

$\Rightarrow \frac{\partial \psi}{\partial t}(x,t) = A\left(\frac{-iE}{\hbar}\right) e^{-i\left(\frac{Et}{\hbar} - \frac{\sqrt{2mE}}{\hbar} x\right)}$

$\Rightarrow \frac{\partial \psi(x,t)}{\partial t} = -\frac{iE}{\hbar} \psi(x,t)$ ——— (12)

Again diff.

$\Rightarrow \frac{\partial^2 \psi(x,t)}{\partial t^2} = \left(\frac{-iE}{\hbar}\right)\left(\frac{-iE}{\hbar}\right) A e^{-i\left(\frac{Et}{\hbar} - \frac{\sqrt{2mE}x}{\hbar}\right)}$

$\Rightarrow \frac{\partial^2 \psi(x,t)}{\partial t^2} = -\frac{E}{\hbar} \psi(x,t)$

Diff. ψ w.r.t x

$\Rightarrow \frac{\partial \psi(x,t)}{\partial x} = -A i\left(\frac{\sqrt{2mE}}{\hbar}\right) e^{-i\left(\frac{Et}{\hbar} - \frac{\sqrt{2mE}\,x}{\hbar}\right)}$

$\Rightarrow \frac{\partial \psi}{\partial x} = i\frac{\sqrt{2mE}}{\hbar} A e^{-i\left(\frac{Et}{\hbar} - \frac{\sqrt{2mE}x}{\hbar}\right)}$

$\Rightarrow \frac{\partial \psi(x,t)}{\partial x} = i\frac{\sqrt{2mE}}{\hbar} \psi(x,t)$

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Again diff. ψ w.r.t x

$$\frac{\partial^2\psi}{\partial x^2} = i^2 \frac{2mE}{\hbar^2} A e^{-i\left(\frac{Et}{\hbar} - \frac{\sqrt{2mE}}{\hbar}x\right)}$$

$$\Rightarrow \frac{\partial^2\psi}{\partial x^2} = -\frac{2mE}{\hbar^2}\psi(x,t) \quad \text{---} \quad (13)$$

Multiplying eqn (12) by '$i\hbar$' & eqn (13) by $\frac{-\hbar^2}{2m}$, we get

$$\Rightarrow i\hbar\frac{\partial\psi}{\partial t} = E\psi(x,t) \quad \text{---} \quad (14)$$

$$\Rightarrow \frac{-i^2\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = E\psi(x,t) \quad \text{---} \quad (15)$$

Comparing eqn (14) and (15)

$$\boxed{i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}} \quad \text{---} \quad (16)$$

eqn (16) is Schrodinger's equation for free particle in 1-D. It plays same role in quantum mechanics as newton's 2nd law in classical mechanics.

Characteristics of Schrodinger's eqn:

The 1-D schrodinger's eqn for a free particle of mass m is given by,

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} \quad \text{---} \quad (17)$$

1. Above eqn reveals that $\frac{\partial\psi}{\partial t}$ and $\frac{\partial^2\psi}{\partial x^2}$ occurs only in the first power i.e linearly. This implies that not only harmonic waves of the form $\psi(x,t) = Ae^{-i(\omega t - kx)}$.

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are the solutions of eqn (17). but any linearly combination or superposition of harmonic waves, such as

$$\psi(x,t) = \int A\, e^{-i(\omega t - kx)}\, dx \quad \text{---(18)}$$

are also the soln of eqn (17)

Eqn (17) represent a wave packet hence schrodinger eqn also has perfectly good wave packet soln.

2. the eqn (17) is of the 1st order in time implies that if ψ is known at the some point ($\vec{r}$) at initial time 't0' then at any time 't'. ψ can be determined.

3. All the partial diff. eqn of classical physics contains real parameters but schrodingers wave eqn contain the imaginary unit(i).

4. The wave function $\psi(\vec{r},t)$ representing the matter wave must be complex function of x & t.

5. The wave eqn (17) is consistent with De-broglie's hypothesis and correspondence principle.

One - dimension time dependent schrodinger Eqn:-

Case (i) (when the particle is free)

Consider a particle of mass 'm' moving with velocity $\vec{v}$, along x dirn. the

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velocity $\vec{v}$ is a small as compared to speed of light c. the wave function associated with the particle is given by

$$\psi(x,t) = A e^{-i(\omega t - Kx)}$$

where, A = const.

$$K = \frac{\omega}{v} = \frac{2\pi\nu}{\nu\lambda} = \frac{2\pi}{\lambda} = K$$

If λ be the wave length, then from de broglie's theory,

$$p = \frac{h}{\lambda} = \hbar K, \quad K = \frac{2\pi}{\lambda} = \frac{p}{\hbar}$$

If 'p' be the momentum of the particle then Kinetic energy (K.E)

$$= \frac{p^2}{2m} = \frac{\hbar^2 K^2}{2m} = h\nu = \hbar\omega$$

$$\omega = \frac{E}{\hbar}$$

The wave function interms of momentum,

$$\Rightarrow \psi(x,t) = A e^{i\left(\frac{P_x x}{\hbar} - \frac{Et}{\hbar}\right)}$$

$$\Rightarrow \psi(x,t) = A e^{i/\hbar (P_x x - Et)} \qquad \text{---------- (19)}$$

eqn (19) is a plane continous simple Harmonic wave eqn associated with a particle having momentum P_x and energy E moving +ve x dirn.

diff. eqn (19) w.r.t x

$$\Rightarrow \frac{\partial\psi}{\partial x} = A\frac{i}{\hbar} P_x e^{i/\hbar (P_x x - Et)}$$

$$\Rightarrow \frac{\partial\psi}{\partial x} = \frac{i}{\hbar} P_x \psi(x,t). \qquad \text{---------- (20)}$$

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Again, differentiating,

$$\Rightarrow \frac{\partial^2\psi}{\partial x^2} = \frac{i^2}{\hbar^2} p_x^2 \psi(x,t)$$

$$\Rightarrow \frac{\partial^2\psi}{\partial x^2} = -\frac{p_x^2}{\hbar^2}\psi(x,t) \quad \text{——— (21)}$$

$$\Rightarrow p_x^2 \psi(x,t) = -\frac{\partial^2\psi}{\partial x^2}\hbar^2 \quad \text{——— (22)}$$

diff. eqn (19) w.r.t t

$$\Rightarrow \frac{\partial\psi}{\partial t} = A\frac{i}{\hbar}(-E)\, e^{i/\hbar(p_x x - Et)}$$

$$\Rightarrow \frac{\partial\psi}{\partial t} = -\frac{iE}{\hbar}\psi(x,t)$$

$$\Rightarrow \frac{\partial\psi}{\partial t} = \frac{E}{i\hbar}\psi(x,t)$$

$$\Rightarrow E\psi = i\hbar\frac{\partial\psi}{\partial t} \quad \text{——— (23)}$$

We know, $E = \frac{p_x^2}{2m}$

$$\Rightarrow p_x^2\psi = 2mi\hbar\frac{\partial\psi}{\partial t} \quad \text{——— (24)}$$

Comparing eqn (22) and (24)

$$\Rightarrow -\hbar^2\frac{\partial^2\psi}{\partial x^2} = 2mi\hbar\frac{\partial\psi}{\partial t}$$

$$\Rightarrow \frac{-\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = i\hbar\frac{\partial\psi}{\partial t} \quad \text{——— (25)}$$

eqn (25) is the 1-D time dependent schrodinger's eqn of a free particle of mass m.

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Since, it doesn't contain momentum (P_x), K.E (E), wavenumber (k), frequency (ν). So it can represent any of the component wave of the wave packet representing the particle.

Case - II

When the particle is acted upon by a force field derivable from a particle (V_x).

Let a particle of mass 'm' moves along x-direction with momentum P_x in a force field derivable from the potential V_x.

total energy,

$$E = \frac{P_x^2}{2m} + V_x$$

multiply by ψ,

$$\rightarrow E\psi = \frac{P_x^2}{2m}\psi + V\psi \quad \text{---------- (26)}$$

The wave function of the particle is given by,

$$\psi(x,t) = A e^{-i/\hbar (P_x x - Et)}$$

$$\rightarrow \frac{\partial \psi}{\partial x} = \frac{i}{\hbar} P_x \psi$$

$$\Rightarrow \frac{\partial^2 \psi}{\partial x^2} = -\frac{P_x^2}{\hbar} \psi$$

$$\Rightarrow P_x^2 \psi = -\hbar^2 \frac{\partial^2 \psi}{\partial x^2}$$

$$\Rightarrow \frac{\partial \psi}{\partial t} = -\frac{iE}{\hbar} \psi$$

$$\rightarrow \frac{\partial \psi}{\partial t} = \frac{E}{\hbar i} \psi$$

$$E\psi = i\hbar \frac{\partial \psi}{\partial t}$$

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putting in eqn (26)

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V\psi = i\hbar\frac{\partial\psi}{\partial t} \quad \text{---(27)}$$

It is also time dependent 1-D Schrodinger eqn for a particle moving under the action of a conservative force field derivable from Vx.

Time dependent & Time Independent Part of the one-dimensional wave eqn:-

The Schrodinger time dependent eqn for a particle moving along +ve x-dirn potential field V is given by,

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V\psi = i\hbar\frac{\partial\psi}{\partial t} \quad \text{---(28)}$$

this eqn is a partial differential eqn of two variable x & t. So we can write

$$\psi(x,t) = u(x)f(t) \quad \text{---(29)}$$

$$\frac{\partial\psi}{\partial x} = f\frac{\partial u}{\partial x}$$

$$\Rightarrow \frac{\partial^2\psi}{\partial x^2} = f\frac{\partial^2 u}{\partial x^2}$$

$$\frac{\partial\psi}{\partial t} = u\frac{\partial f}{\partial t}$$

Then eqn (28) becomes,

$$\Rightarrow \frac{-\hbar^2}{2m}f\frac{\partial^2 u}{\partial x^2} + Vuf = i\hbar u\frac{\partial f}{\partial t}$$

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Dividing by $u f$

$$\frac{-\hbar^2}{2m}\frac{1}{u}\cdot\frac{\partial^2 u}{\partial x^2}+V=\frac{i\hbar}{f}\frac{\partial f}{\partial t} \quad (30)$$

Since LHS of eqn (30) is function of x & RHS is function of t only, so LHS is the time independent part while RHS is the time dependent part of schrodinger's eqn (28). As x & t are independent variables each side of eqn (30) may be equal to a constant say total energy E.

$$\frac{-\hbar^2}{2m}\frac{1}{u}\frac{\partial^2 u}{\partial x^2}+V=\frac{i\hbar}{f}\frac{\partial f}{\partial t}=E \quad (31)$$

Time dependent Part:-

$$i\hbar\frac{1}{f}\frac{\partial f}{\partial t}=E$$

$$\Rightarrow i(i)\hbar\frac{1}{f}\frac{\partial f}{\partial t}=Ei$$

$$\Rightarrow \int\frac{\partial f}{f}=-\int\frac{iE}{\hbar}dt$$

Integrate,

$$\Rightarrow \log f=\frac{-iE}{\hbar}t+\log C$$

$$\Rightarrow \log(f/C)=-\frac{iE}{\hbar}t$$

$$\Rightarrow (f/C)=e^{\frac{-iEt}{\hbar}}$$

$$\Rightarrow \boxed{f=Ce^{\frac{-iEt}{\hbar}}} \quad (32)$$

eqn (32) represents time dependent part of the soln $\psi(x,t)$ of the schrodinger's eqn.

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Time Independent part:-

$$\frac{-\hbar^2}{2m}\frac{1}{u}\frac{\partial^2 u}{\partial x^2} + V = E$$

$$\Rightarrow \frac{-\hbar^2}{2m}\frac{\partial^2 u}{\partial x^2} + uV = Eu$$

$$\Rightarrow -\frac{\partial^2 u}{\partial x^2} = (E-V)\,u\,\frac{2m}{\hbar^2}$$

$$\Rightarrow \frac{\partial^2 u}{\partial x^2} + (E-V)\,u\,\frac{2m}{\hbar^2} = 0 \qquad (33)$$

The soln of the time dependent Schrodingers eqn is

$$\psi(x,t) = u(x)\,f(t).$$

$$\psi(x,t) = c\,u(x)\,e^{-\frac{2\pi i E}{\hbar}t}$$

$$\Rightarrow \psi(x,t) = u(x)\,e^{-2\pi i \omega t} \qquad (34)$$

where,

$$E = h\nu = \frac{h}{2\pi}2\pi\nu = \hbar\omega \quad \text{and} \quad c = 1$$

eqn (34) is the particular soln of the time dependent schrodingers eqn.

If $\psi_1(x,t)$, $\psi_2(x,t)$ --- $\psi_n(x,t)$ be a set of particular soln of a system corresponding to energy $E_1, E_2 \cdots E_n$, then the general soln of the wave eqn is given by

$$\psi(x,t) = \psi_1(x,t) + \psi_2(x,t) + \cdots + \psi_n(x,t)$$

$$\psi(x,t) = c_1 u_1 e^{-2\pi i E_1 t/\hbar} + c_2 u_2 e^{-2\pi i E_2 t/\hbar} + \cdots + c_n u_n e^{-2\pi i E_n t/\hbar}$$

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$$= \sum_{n=1}^{n} C_n \psi_n(x)\, e^{-i\omega_n t}$$

$$\boxed{\psi(x,t) = \sum_{1}^{n} C_n \psi_n(x)\, e^{-i\omega_n t}} \quad (35)$$

The general soln given by eqn (35) doesn't satisfy schroedingers time dependent eqn (33).

Three-Dimensional schrodinger's eqn:

Consider A particle of mass 'm' moving along any direction with reference to the cartesian co-ordinate in a force field

$$\vec{F} = -\nabla V$$

where, V = potential

∇ = function of x, y, z

If V independent of time so the force field is conservative.

According to de-broglies hypothesis the particle is associated with a wave packet represented by the wave function,

$$\psi(\vec{r},t) = A\, e^{i/\hbar\,(\vec{p}\cdot\vec{r} - Et)} \quad (36)$$

p = momentum

E = energy $= \frac{p^2}{2m} + V(\vec{r})$

where, $p^2 = \hat{i}p_x^2 + \hat{j}p_y^2 + \hat{k}p_z^2$

$$\Rightarrow E\psi = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)\psi + V(\psi) \quad (37)$$

eqn (36) can be written as

$$\psi(\vec{r},t) = A\, e^{i/\hbar\,[(p_x x + p_y y + p_z z) - Et]} \quad (38)$$

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$$\Rightarrow \frac{\partial \psi}{\partial x} = A \frac{i}{\hbar} p_x e^{i/\hbar (p_x x + p_y y + p_z z)} \quad \text{--- (1)}$$

$$\Rightarrow \frac{\partial \psi}{\partial x} = \frac{i}{\hbar} p_x \psi \quad \text{--- (39)}$$

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{-p_x^2}{\hbar^2} \psi \quad \text{--- (40)}$$

$$\Rightarrow p_x^2 \psi = -\hbar^2 \frac{\partial^2 \psi}{\partial x^2} \quad \text{--- (41)}$$

$$\Rightarrow p_y^2 \psi = -\hbar^2 \frac{\partial^2 \psi}{\partial y^2} \quad \text{--- (42)}$$

$$\Rightarrow p_z^2 \psi = -\hbar^2 \frac{\partial^2 \psi}{\partial z^2} \quad \text{--- (43a)}$$

$$\frac{\partial \psi}{\partial t} = \frac{-iE}{\hbar} A e^{i/\hbar (\vec{p} \cdot \vec{r} - Et)}$$

$$\frac{\partial \psi}{\partial t} = \frac{-iE}{\hbar} \psi$$

$$\Rightarrow E\psi = \frac{-\hbar}{i} \frac{\partial \psi}{\partial t}$$

$$\Rightarrow E\psi = -\hbar i \frac{\partial \psi}{\partial t} \quad \text{--- (44)}$$

using above in eqn (41, 42, 43) — (37)

$$\frac{1}{2m} (-\hbar^2) \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + V\psi = i\hbar \frac{\partial \psi}{\partial t}$$

$$\Rightarrow \boxed{\frac{-\hbar^2}{2m} \nabla^2 \psi + V\psi = i\hbar \frac{\partial \psi}{\partial t}} \quad \text{--- (45)}$$

from (41) & (45)

$$\left(\frac{-\hbar^2}{2m} \nabla^2 + V \right) \psi = E\psi$$

$$\Rightarrow H\psi = E\psi$$

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where,

$H = \frac{-\hbar^2}{2m}\nabla^2 + V$ - Hamiltonian factor

eqn (45) is called 3-D schrodingers eqave eqn which is of 2nd order in space and 1st order in time.

For a free particle V is '0'.

so from eqn (45)

$$\frac{-\hbar^2}{2m}\nabla^2\psi = i\hbar\frac{\partial\psi}{\partial t} = E\psi \quad (46)$$

which is 3-D schrodingers wave eqn of a free particle moving in 3-D.

Time dependent and time independent part:-

If $u(\vec{r})$ and $f(t)$ be the time indepnd and time dependent part of $\psi(\vec{r},t)$, then we can write

$$\psi(\vec{r},t) = u(\vec{r}).f(t) \quad (47)$$

eqn (46) becomes,

$$-\frac{\hbar^2}{2m}f\left(\frac{\partial^2 u}{\partial x^2}+\frac{\partial^2 u}{\partial y^2}+\frac{\partial^2 u}{\partial z^2}\right)+V(uf) = i\hbar u\frac{\partial f}{\partial t}$$

Dividing by uf

$$\Rightarrow \frac{-\hbar^2}{2m}\frac{1}{u}\left(\frac{\partial^2 u}{\partial x^2}+\frac{\partial^2 u}{\partial y^2}+\frac{\partial^2 u}{\partial z^2}\right)+V = i\hbar\frac{1}{f}\frac{\partial f}{\partial t} \quad (48)$$

Since L.H.S of above eqn is function of space-coordinate and R.H.S is function of time. So each side may be equal

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Constant. Say E: where E is the total energy which is constant.

$$\therefore -\frac{\hbar^2}{2m}\frac{1}{u}\left(\frac{\partial^2 u}{\partial x^2}+\frac{\partial^2 u}{\partial y^2}+\frac{\partial^2 u}{\partial z^2}\right)+V = \frac{i\hbar}{f}\frac{\partial f}{\partial t} = E$$

$$\Rightarrow \boxed{\frac{-\hbar^2}{2m}\frac{1}{u}\left(\frac{\partial^2 u}{\partial x^2}+\frac{\partial^2 u}{\partial y^2}+\frac{\partial^2 u}{\partial z^2}\right)+V = i\hbar\frac{1}{f}\frac{\partial f}{\partial t} = E} \quad (49)$$

Time dependent Path:-

We have, $i\hbar\frac{1}{f}\frac{\partial f}{\partial t} = E$

$\Rightarrow \frac{\partial f}{f} = \frac{E}{i\hbar}\,dt$

$\Rightarrow \log f = \frac{E}{i\hbar}t + \log C$

$\Rightarrow \log(f/C) = -\frac{i}{\hbar}Et$

$\Rightarrow f/C = e^{-i/\hbar(Et)}$

$\Rightarrow \boxed{f = C e^{-i/\hbar Et}} \quad (50)$

where C = const.

eqn (50) is the time dependent path of the Schrodinger's eqn.

Time Independent path:-

$$\Rightarrow \frac{-\hbar^2}{2m}\frac{1}{u}\left(\frac{\partial^2 u}{\partial x^2}+\frac{\partial^2 u}{\partial y^2}+\frac{\partial^2 u}{\partial z^2}\right)+V = E$$

$$\Rightarrow \frac{-\hbar^2}{2m}\left(\frac{\partial^2 u}{\partial x^2}+\frac{\partial^2 u}{\partial y^2}+\frac{\partial^2 u}{\partial z^2}\right)+uV = Eu$$

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$$\Rightarrow \frac{-\hbar^2}{2m}(\nabla^2 u) + Vu = Eu \quad \text{(51)}$$

$$\Rightarrow \frac{-\hbar^2}{2m}\nabla^2 u = (E-V)u$$

$$\Rightarrow \nabla^2 u = -\frac{2m}{\hbar^2}(E-V)u$$

$$\therefore \Rightarrow \boxed{\nabla^2 u + \frac{2m}{\hbar^2}(E-V)u = 0} \quad \text{(52)}$$

for a force particle, $V=0$

eqn (52) becomes,

$$\nabla^2 u + \frac{2m}{\hbar^2}Eu = 0 \quad \text{(53)}$$

The 3-D wave function is

$$\varphi(\vec{r},t) = u(\vec{r})\cdot f(t)$$

$$= c\,u(\vec{r})\cdot e^{-\frac{iEt}{\hbar}}$$

$$= c\,u(\vec{r})\,e^{-i\omega t} \quad (\because E = \hbar\omega) \quad \text{(54)}$$

Physical Interpretation of the wave fun $\varphi(\vec{r},t)$

To understand physical interpretation, several time we have seen that the wave associated with particle are represented by $\varphi(\vec{r},t)$ called wave function. Regarding $\varphi(\vec{r},t)$, several question arise,

(i) Is $\varphi(\vec{r},t)$ measurable quantity.

(ii) What does $\varphi(\vec{r},t)$ describe

(iii) What features of the particle is related to $\varphi(\vec{r},t)$?

Always the properties of wave represented by $\varphi(\vec{r},t)$ and the way in which $\varphi(\vec{r},t)$ used in the calculation be known. Satisfying answer of the question Born

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expected. Still the wave function $\psi(\vec{r},t)$ describe the space time behaviour of the particle is such the its magnitude is large in the region where the probability of finding the particle is large in the other region where the probability is small. the magnitude of $\psi(\vec{r},t)$ is small.

Thus $\psi(\vec{r},t)$ may be regarded as the probability of finding the particle around a particular point in space in space. Again probability is a real and numerical negative. whereas $\psi(\vec{r},t)$ is complex function we shall assume that the quantity is proportional to the

$$|\psi(\vec{r},t)|^2 d^3r = \psi^*(\vec{r},t)\,\psi(\vec{r},t)\,d^3r \quad \text{---(55)}$$

Probability of finding the particle in volume arrangement d^3r around the point r in time t. Hence $\psi^*(\vec{r},t)$ is the complex conjugate of $\psi(\vec{r},t)$. total probability of finding particle is

$$\psi(\vec{r},t) \cdot \alpha \int_{-\infty}^{\infty} |\psi(\vec{r},t)|^2 d^3r$$

The position probability density is defined as

$$f(\vec{r},t) = \frac{|\psi(\vec{r},t)|}{\int_{-\infty}^{\infty} |\psi(\vec{r},t)|^2 . d^3r} \quad \text{---(56)}$$

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Thus according to max born, the most direct physical interpretation of the wave function $\psi(\vec{r},t)$ is the its modulus square determines.

probability density of the particle in space since $|\psi(\vec{r},t)|^2$ is a positive quantity, $\rho(\vec{r},t)$ is always +ve. So the total probability of finding the particle anywhere in the space is $\rho(\vec{r},t)$.

$$\rho(\vec{r},t) = \int_{-\infty}^{\infty} \rho(\vec{r},t)\, d^3r = \frac{\int_{-\infty}^{\infty} \psi(\vec{r},t)^2 d^3r}{\int_{-\infty}^{\infty} |\psi(\vec{r},t)|^2 d^3r} \leq 1 \quad (57)$$

Normalisation of wave function:

The 3-D time independent Schrodinger eqn of a particle is given by

$$\nabla^2 u + \frac{2m}{\hbar^2}(E - V)u = 0 \quad (58)$$

The Schrodinger wave eqn is linear and homogeneous in ψ and its derivatives $\frac{\partial^2\psi}{\partial t^2}$ and $\frac{\partial\psi}{\partial t}$ i.e. any const multiplied by a constant then the resulting wave function be the solution. To avoid this arbitrariness it is necessary to impose normalisation condition.

Let us $\psi(\vec{r},t)$ is a solution of schrodinger eqn (58) and $\int_{-\infty}^{\infty} |\psi(\vec{r},t)|^2 d^3r = N^2$ (59)

where, $|\psi_1(\vec{r},t)|^2 = \psi_1^*(\vec{r},t) \cdot \psi_1(\vec{r},t)$

is a positive no. and so also thus integer n^2 is real positive no. and is

called normalisation of $\psi(\vec{r},t)$.

Now consider another wave function $\psi(\vec{r},t)$ which is related to $\psi_1(\vec{r},t)$ by the relation.

$$\psi(\vec{r},t) = \frac{1}{N}\psi_1(\vec{r},t) \quad (60)$$

where $\psi(\vec{r},t)$ is a sol^n of eq^n (58) and differs from $\psi_1(\vec{r},t)$ by a constant factor $\frac{1}{N}$.

Using (60) in (59)

$$\int_{-\infty}^{\infty} N^2 |\psi(\vec{r},t)|^2 d^3r = N^2$$

$$\Rightarrow \int_{-\infty}^{\infty} |\psi(\vec{r},t)|^2 d^3r = 1 \quad (61)$$

The wave function which is satisfied eq^n (61) is said to be normalised. Hence a normalised wave function must had unit norm.

Since N in eq^n (60) must be finite as $|\psi(\vec{r},t)|^2$ is finite and $|\psi(\vec{r},t)|^2$ tends to zero as r tends to infinity.

eq^n (61) gives the condition of normalisation for 1-D motion.

$$\int_{-\infty}^{\infty} |\psi(x,t)|^2 dx = 1$$

$$\Rightarrow \int_{-\infty}^{\infty} \psi^*(x)\psi(x)dx = 1 \quad (62)$$

This is normalisation condition.

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Orthogonality of wave function:-

Consider a set of wave function satisfy schrodinger wave eqn $\psi_1(\vec{r}), \psi_2(\vec{r}) \cdots \psi_n(\vec{r})$ such that any two function $\psi_m(\vec{r})$ and $\psi_n(\vec{r})$ in the set satisfied the condn

$$\int \psi_m^*(\vec{r})\, \psi_n(\vec{r})\, d\vec{\tau} = 0 \qquad (m \neq n) \qquad (63)$$

then the function in the set are set to be orthogonal in analogy be the condn of orthogonal if two vector,

$$\psi_m^*(\vec{r}) \cdot \psi_m(\vec{r})\, d\tau = 1 \qquad (m = n) \qquad (64)$$

then each function is normalised. then the set of function under consideration is called orthogonal set of wave function.

$$\boxed{\int \psi_m^*(\vec{r}) \cdot \psi_n(\vec{r})\, d\tau = \delta_{mn}} \qquad (65)$$

$\delta_{mn} = 1$, $m = n$

$\delta_{mn} = 0$, $m \neq n$.

If the normalised orthogonal wavefeen are single value, continuous, finite throughout the entire space of the system & satisfy schrodinger's wave eqn then they can be present at a series of order orthogonal wave function of the same variable. If $\phi(\vec{r})$ have the above properties and

$$\phi_1(\vec{r}), \phi_2(\vec{r}) \cdots \phi_n(\vec{r}).$$

are the set of mutual orthogonal wave function.

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$$\psi(\vec{r}) = c_1\phi_1 + c_2\phi_2 + \cdots + c_n\phi_n \quad (66)$$

where $c_1, c_2 \cdots c_n$ are const.

multiplied eqn (66) by ϕ_m^* and integrate over all space.

$$\int \phi_m^* \psi(\vec{r})\, dz = c_1 \int \phi_m^* \phi_1\, dz + c_2 \int \phi_m^* \phi_2 dz + \cdots + c_m \int \phi_m^* \phi_n\, dz$$

$$= 0 + c_m = c_m \quad (67)$$

All terms are vanished and the last term exist.

The value of the expression coefficient, $c_1, c_2 \cdots c_m$ can be found out using eqn (67)

The complex conjugate of eqn (66)

$$\psi^* = c_1^* \phi_1^* + c_2^* \phi_2^* + \cdots c_m^* \phi_m^* + \cdots \quad (68)$$

$$\Rightarrow \psi^* \cdot \psi = [c_1^* \phi_1^* + c_2^* \phi_2^* + \cdots + c_m^* \phi_m^*] \times (c_1\phi_1 + c_2\phi_2 + \cdots + c_m\phi_m)$$

$$\Rightarrow \int \psi^* \cdot \psi = \int (c_1^* \cdot \phi_1^* + c_2^* \phi_2^* + \cdots + c_m^* \phi_m^*) \times (c_1\phi_1 + c_2\phi_2 + \cdots + c_m\phi_m)\, dz \quad (69)$$

$$\Rightarrow 1 = c_1^* c + c_2^* c_2 + \cdots + c_m^* c_m$$

As $\int \phi_m^* \cdot \phi_n\, dz = 0$ $m \neq n$

$= 1$ $m = n$

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$\Rightarrow 1 = \sum_m C_m^* C_m$

thus the wave function $\psi(\vec{r},t) = \sum_m C_m \phi_m$ satisfied the Schrodinger's eqn.

Stationary state :-

If the probability density $\rho = \psi^* \psi$ is independent of time for a particular state, then the state is called stationary state.

In general eqn of 3-D time dependent schrodinger eqn is given by

$$\psi(\vec{r},t) = \sum_n C_n \psi_n \cdot e^{-\frac{i}{\hbar} E_n t} \quad \text{---(70)}$$

$$\psi^*(\vec{r},t) = \sum_m C_m^* \psi_m^* \cdot e^{\frac{i}{\hbar} E_m t}$$

The probability density is

$$\rho(\vec{r},t) = \psi^*(\vec{r},t) \cdot \psi(\vec{r},t)$$

$$= \sum_n C_n^* C_n \psi_n^* \psi_n + \sum_m \sum_n C_m^* C_n \psi_m^* \psi_n \, e^{\frac{i}{\hbar}(E_m - E_n)t} \quad \text{---(71)}$$

eqn (71) shows that $\rho(\vec{r},t)$ depends on time and the state expressed by eqn (70) is not a stationary state. But $\rho(\vec{r},t)$ can be independent of t, but C_n's are zero for all value except or value E_k. In such case the wave function will contain only single term and will be represented by $\psi(\vec{r},t) = C_k \psi_k e^{-iE_k t/\hbar}$ ---(72) for

this energy state E_k.

$$\psi^*(\vec{r},t)\cdot\psi(\vec{r},t) = C_k^* C_k \psi_k^* \psi_k = \rho(\vec{r}) \quad \text{---(3)}$$

eqn (3) is independent of time t. And the energy state represented by E_k is called stationary state. The eqn given by eqn (3) is called stationary state function being independent of time.

Conservation of Probability :-

We know that according to the Probability interpretation of the normalised wavefunction the probability of finding the particle over all space is unity. This implies that particle must be found some where in space. If the particle doesn't decay or disappear in some other way then the above statement must be true at all values of time. In other words the total probability must be conserved i.e $\int |\psi(\vec{r},t)|^2$ must be independent of time.

$$\frac{\partial}{\partial t}\int |\psi(\vec{r},t)|^2 \, d\tau = \int \frac{\partial}{\partial t}|\psi(\vec{r},t)|^2 \, d\tau$$

$$= \int \frac{\partial \rho}{\partial t}(\vec{r},t)\, d\tau = 0$$

where, $|\psi(\vec{r},t)|^2 = \rho(\vec{r},t)$ ---(1)

The 3-D time dependent schrodinger eqn is given by

$$i\hbar \frac{\partial \psi}{\partial t} = \frac{-\hbar^2}{2m}\nabla^2\psi + V\psi \quad \text{---(2)}$$

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Now replacing ψ by its Complex conjugate,

$$-i\hbar \frac{\partial \psi^*}{\partial t} = \frac{-\hbar^2}{2m} \nabla^2 \psi^* + V\psi^* \quad \text{---(3)}$$

Multiplying eqn (2) by ψ^* and (3) by ψ.

$$i\hbar \frac{\partial \psi}{\partial t} \psi^* = \frac{-\hbar^2}{2m} \nabla^2 \psi \psi^* + \psi^* V \psi \quad \text{---(4)}$$

$$i\hbar \frac{\partial \psi^*}{\partial t} \psi = \frac{-\hbar^2}{2m} \psi \nabla^2 \psi^* + \psi V \psi^* \quad \text{---(5)}$$

subtracting (5) from (4)

$$i\hbar \left(\psi^* \frac{\partial \psi}{\partial t} + \psi \frac{\partial \psi^*}{\partial t}\right) = \frac{-\hbar^2}{2m} \left(\psi^* \nabla^2 \psi - \psi \nabla^2 \psi^*\right) \quad \text{---(6)}$$

$$\psi^* \frac{\partial \psi}{\partial t} + \psi \frac{\partial \psi^*}{\partial t} = \frac{-\hbar}{2mi} \left(\psi^* \nabla^2 \psi - \psi \nabla^2 \psi^*\right)$$

(Multiplying $\frac{1}{i}$ by numerator and denominator

$$\Rightarrow \frac{\partial}{\partial t}(\psi^* \psi) = \frac{i\hbar}{2m} \left(\psi^* \nabla^2 \psi - \psi \nabla^2 \psi^*\right)$$

$$\Rightarrow \frac{\partial}{\partial t}(\psi^* \psi) + \frac{i\hbar}{2m} \left(\psi \nabla^2 \psi^* - \psi^* \nabla^2 \psi\right) = 0$$

$$\Rightarrow \frac{\partial}{\partial t}(\psi^* \psi) + \frac{i\hbar}{2m} \left[\frac{\partial}{\partial x}\left(\psi \frac{\partial \psi^*}{\partial x} - \psi^* \frac{\partial \psi}{\partial x}\right) + \right.$$

$$\left. \frac{\partial}{\partial y}\left(\psi \frac{\partial \psi^*}{\partial y} - \psi^* \frac{\partial \psi}{\partial y}\right) + \right.$$

$$\left. \frac{\partial}{\partial z}\left(\psi \frac{\partial \psi^*}{\partial z} - \psi^* \frac{\partial \psi}{\partial z}\right)\right] = 0 \quad \text{---(7)}$$

$$\Rightarrow \frac{\partial}{\partial t} \rho(\vec{r}, t) + \vec{\nabla} \cdot \vec{J}(\vec{r}, t) = 0$$

where $\rho(\vec{r}, t) = \psi^* \psi$ ---(8)

and $\vec{\nabla} \cdot \vec{J} = \frac{\partial J_x}{\partial x} + \frac{\partial J_y}{\partial y} + \frac{\partial J_z}{\partial z}$ ---(9)

where, $J_x = \frac{i\hbar}{2m} \left(\psi \cdot \frac{\partial \psi^*}{\partial x} - \psi^* \cdot \frac{\partial \psi}{\partial x}\right)$ ---(10)

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$$J_y = \frac{\hbar}{2m}\left(\psi \cdot \frac{\partial \psi^*}{\partial y} - \psi^* \frac{\partial \psi}{\partial y}\right) \quad (11)$$

$$J_z = \frac{\hbar}{2m}\left(\psi \cdot \frac{\partial \psi^*}{\partial z} - \psi^* \frac{\partial \psi}{\partial z}\right) \quad (12)$$

Therefore, $\vec{J}(\vec{r},t) = \frac{\hbar}{2m}(\psi \nabla \psi^* - \psi^* \nabla \psi)$ (13)

Now diff. integral of $\rho(\vec{r},t)\,d\tau$ over all space we get,

$$\frac{\partial}{\partial t}\int_\tau \rho(\vec{r},t)\,d\tau = \int_\tau \frac{d}{dt}(\psi^*\psi)\,d\tau = \int_\tau \vec{\nabla}\cdot\vec{J}\,d\tau$$

$$\Rightarrow \frac{\partial}{\partial t}\int_\tau \rho(\vec{r},t)\,d\tau = -\oint_S \vec{J}\cdot d\vec{s} = -\oint_S \vec{J}\cdot\hat{n}\,ds \quad (14)$$

where S is the closed surface enclosing volume τ. Since the volume integral is over all space, the surface is an infinity that $r \to \infty$ is zero. This implies ψ and $\nabla\psi$ vanish at the surface S and J also vanish sufficiently as $r \to \infty$.

$$\oint_S J\cdot\hat{n}\,ds = 0$$

Thus,

$$\frac{\partial}{\partial t}\int_\tau \rho(\vec{r},t)\,d\tau = 0 \quad (15)$$

i.e. means $\int \rho(\vec{r},t)\,d\tau$ is independent of time and satisfies the conservation of total probability.

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Probability Current density :-

From eqn (7)

$\frac{\partial f}{\partial t} + \vec{\nabla} \cdot \vec{J} = 0$ is the familiar eqn of Continuity in hydro-dynamics where 'f' and 'J' represent respectively the density of matter and current density there. In the present Case $f = \psi^* \cdot \psi$ represent the probability density and the probability current density

$$J = \frac{-i\hbar}{2m} (\psi \nabla \psi^* - \psi^* \nabla \psi) \quad \text{(16)}$$

Condn of Admissibility or acceptibility of the wave function.

1. $\psi(\vec{r},t)$ must be finite everywhere in space. this is must because $|\psi(\vec{r},t)|^2 d\tau$ for an infinite decimal volume element $d\tau$ should be between 0 & 1.
2. $\psi(\vec{r},t)$ must be single valued everywhere.
3. ψ and its 1st partial derivatives w.r.t its variable's are continuous. this implies that there must not exist any sudden change in ψ when it's variable's undergues a change.
4. ψ must be square integrable. So that the Integral of it's modulus square is finite.

i.e $I = \int_\tau |\psi|^2 d\tau$ is finite or zero.

5. ψ is zero at any surface at which there is an infinite potential step. the component of $\nabla\psi$ normal to the surface is undetermined.

A wave function which satisfied all the above condition is an admissible wave function or acceptable wave function.

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PROBLEM:

1) Normalised the 1-D wave function given by $\psi(x) = A \sin\frac{\pi x}{l}$ $0 < x < l$
$= 0$ outside.

Sol^n The wave function $\psi(x)$ is said to be normalised if it satisfied:

$$\int_{-\infty}^{\infty} \psi^*(x)\,\psi(x)\,dx = 1$$

The given wave function exist only in the region 0 to L. outside. So

$$\Rightarrow \int_0^l A^* \sin\frac{\pi x}{l} \cdot A \sin\frac{\pi x}{l} \cdot dx = 1$$

$$\Rightarrow |A|^2 \int_0^l \sin^2\frac{\pi x}{l}\,dx = 1$$

$$\Rightarrow |A|^2 \frac{1}{2} \int_0^l \left(1 - \cos\frac{2\pi x}{l}\right) dx = 1$$

$$\Rightarrow \frac{A^2}{2}\left[x - \sin\frac{2\pi x}{l} \cdot \frac{l}{2\pi}\right]_0^l = 1$$

$$\Rightarrow A^2\left[l - \frac{l}{2\pi}(\sin 2\pi - \sin 0)\right] = 2$$

$$\Rightarrow A^2 \times l = 2$$

$$\Rightarrow A^2 = \frac{2}{l} \Rightarrow A = \sqrt{2/l}$$

The Normalise wave function

$$\boxed{\psi(x) = \sqrt{\frac{2}{l}} \sin\frac{\pi x}{l}}$$

2) The wave function of a particle is given by $\psi(x) = C e^{-\alpha x^2}$ $-\infty < x < \infty$. where C and α are constant. Calculate the probability of finding the particle in

Sol?

The given function $\psi(x) = c e^{-\alpha^2 x^2}$

$\psi^*(x) = c^* e^{-\alpha^2 x^2}$

the probability of finding the particle in the region $0 < x < \infty$ is given by

$$P = \int_0^\infty \psi^*(x)\,\psi(x)\,dx$$

$$= \int_0^\infty c^* e^{-\alpha^2 x^2} \cdot c e^{-\alpha^2 x^2}\,dx$$

$$= c^2 \int_0^\infty e^{-\alpha^2 x^2 - \alpha^2 x^2}\,dx$$

$$= c^2 \int_0^\infty e^{-2\alpha^2 x^2}\,dx$$

$$= c^2 \int_0^\infty e^{-2\alpha^2 x^2}\,dx$$

$$\int_0^\infty e^{-\alpha x^2} = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}}$$

$$P = c^2 \frac{1}{2}\sqrt{\frac{\pi}{2\alpha^2}}$$

Now normalise the wave function

$$\int_{-\infty}^{\infty} \psi^*(x) \cdot \psi(x)\,dx = 1$$

$$\Rightarrow \int_{-\infty}^{\infty} |\psi(x)|^2\,dx = 1$$

$$\Rightarrow \int_{-\infty}^{\infty} |c|^2 e^{-2\alpha^2 x^2}\,dx = 1$$

$$\Rightarrow |c|^2 \sqrt{\frac{\pi}{2\alpha^2}} = 1$$

$$\Rightarrow |c|^2 = \sqrt{\frac{2\alpha^2}{\pi}}$$

$$\therefore P = \sqrt{\frac{2\alpha^2}{\pi}} = \frac{1}{2}\sqrt{\frac{\pi}{2\alpha^2}}$$

$$\boxed{P = 1/2}$$ (Ans).

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2. the wave function of a particle confined to a box of length 'l' is,

$\psi(x) = \left(\frac{2}{l}\right)^{1/2} \sin\frac{\pi x}{l}$ in the region $0<x<l$ and '0' everywhere else. Calculate the probability of finding the particle in the region $0<x<l/2$.

A) the probability of finding the particle in interval Δx at a distance 'x'.

$$P(x)\,\delta x = \psi^*(x)\,\psi(x)\,\delta x$$

$$\psi(x) = \left(\frac{2}{l}\right)^{1/2} \sin\frac{\pi x}{l} = \psi^*(x)$$

Therefore,

$$P(x)\,\delta x = \frac{2}{l}\sin^2\frac{\pi x}{l}\,\delta x$$

Total probability in the region $0<x<l/2$

$$P = \int_0^{l/2} P(x)\,dx = \frac{2}{l}\int_0^{l/2} \sin^2\frac{\pi x}{l}\,dx$$

$$= \frac{2}{l}\cdot\frac{1}{2}\int_0^{l/2}\left(1-\cos\frac{2\pi x}{l}\right)dx$$

$$= \frac{1}{l}\left[\frac{l}{2} - \frac{\sin\frac{2\pi x}{l}}{2\pi/l}\right]_0^{l/2}$$

$$= \frac{1}{l}\left(\frac{l}{2}-0\right) = \frac{1}{2}$$

4. Calculate the normalisation constant for a wave function at $t=0$, given by

$\psi(x) = A\, e^{-\frac{a^2x^2}{2}} \cdot e^{ikx}$.

Determine the probability density and probability current density.

A)

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